Chlorinated Dimers Present in Several Technical Chlorophenols Used as Fungicides*

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Dimers in Pentachlorophenol

The presence of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin in 2,4,5-trichlorophenoxy acid esters was shown to originate from 2,4,5-trichlorophenol used in industrial processes. The dimerization is thought to occur when the phenol is produced from the corresponding tetrachlorobenzene by the action of alkali.

Logically all products originating from chlorinated benzenes treated with alkali are possible sources of chlorinated dibenzo-*p*-dioxins (chlorinated dioxins). We have therefore investigated the presence of chlorinated dioxins in some pentachlorophenol formulations (*1*). The first result obtained was that the content of the expected octachlorodibenzo-*p*-dioxin in one formulation was 1000 ppm (1 g/kg). However, the phenol-free extract was treated with diazomethane and reinjected into the gas chromatograph. Despite the fact that a dioxin cannot react with diazomethane, the octachlorodioxin content decreased to 50 ppm. At the same time, two new peaks appeared in the chromatogram. The compounds corresponding to these peaks were identified by means of mass spectrometry to be the methyl ethers of two isomeric nonachlorohydroxydiphenyl ethers. The phenol corresponding to one of these ethers was later on proved to produce the octachlorodioxin in the gas chromatographic column. Thus the first (high value) of octachlorodioxin was the sum of the true dioxin and its precursor, the hydroxydiphenyl ether. This compound was consequently given the name of predioxin. In the other diphenyl ether the hydroxy groups were not in a position allowing ring closure, and it was therefore given the name of isopredioxin. The highest values found in the formulations investigated are given in parentheses in eq. (1).

In addition to these three substances, also present was an analogous series originating from the reaction of one molecule of pentachlorophenol with one molecule of the impurity tetrachlorophenol. The corresponding values for the above mentioned formulation were D7, 870 ppm; PD7, 1300 ppm; and iso-PD7, 1200 ppm. The total content of these dimeric substances was thus 10 g/kg.

Dimers in 2,4,6-Tri- and 2,3,4,6-Tetrachlorophenols from Direct Chlorination of Phenol

Chlorinated phenols are also produced by chlorination of phenol by means of an iron salt as catalyst (*2*). No alkali is used in

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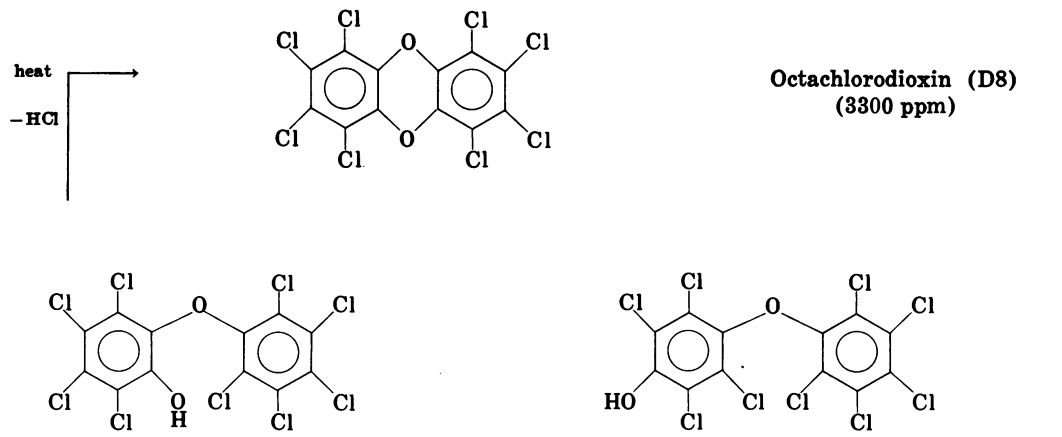
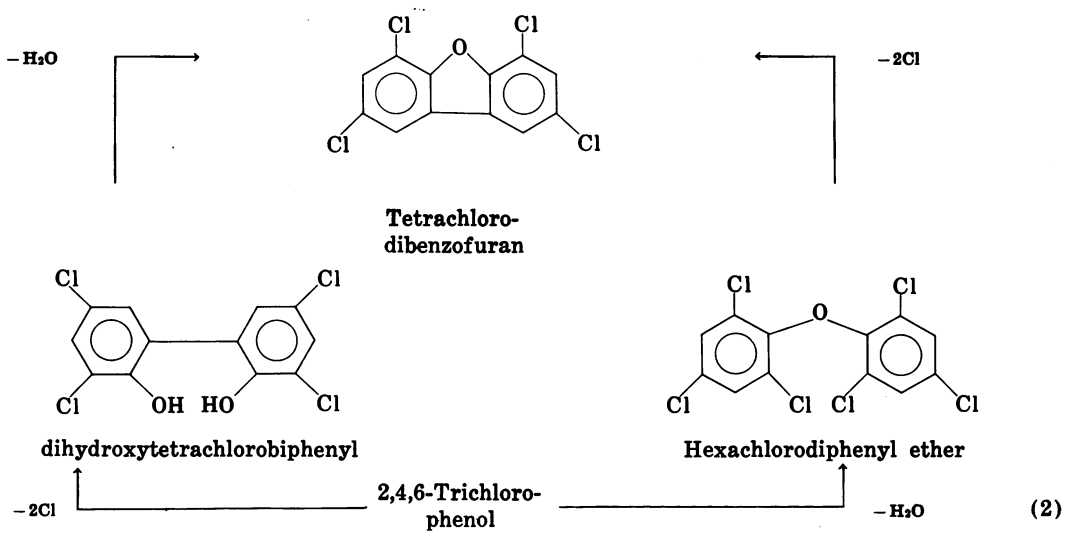


(1)

this process, but nevertheless dimers are formed. The amount is in some formulations up to 50 g/kg. In contrast to the products formed in the alkali process above, no dioxin was detected, but high amounts of both predioxins and isopredioxins were found. The most probable predioxins expected are the precursors to tetra- and hexachlorodibenzo-*p*-dioxin, respectively, and the corresponding isopredioxins.



(2)

Thus it seems that heat and/or alkali favor a ring closure resulting in the formation of a dioxin.

However, chlorinated dihydroxy biphenyls not known to be found earlier have been detected in formulations produced via direct chlorination. These substances are formed by dechlorination of two molecules of phenol, and may produce chlorinated dibenzofurans through dehydration. This reaction may be responsible for the presence of the dibenzofurans. An alternative route may be de-

chlorination of the chlorinated diphenyl ethers, also found in these formulations.

Pyrolysis of Pentachlorophenol

We have recently demonstrated that on burning of pentachlorophenol-impregnated sawdust polychlorinated dibenzo-*p*-dioxins are formed. Thus, from 3.7 g of sawdust containing 73 mg of pentachlorophenol, 0.73 mg of heptachlorodibenzo-*p*-dioxin and 0.47 mg of the octachloro homolog were isolated, which constitutes about 2% of the theoretical yield formed under conditions simulating those practically used in saw mills. The sawdust was burned in a Soxhlet apparatus with air blown in through the bottom; the evolved gases passed through the condenser to two coupled washing flasks containing chloroform. When the sawdust had disappeared the whole system was rinsed simply by using the Soxhlet apparatus in the normal manner, ether–chloroform (1:1) being used for the extraction. In this last step the cooling water was circulated in another condenser placed on top of the first. Half of the pyrolysis products appeared in the condenser and the other half in the washing flasks.

Chlorinated Dibenzofurans in Technical Pentachlorophenate

Highly chlorinated dibenzofurans have been detected in sludge taken from a dipping tank containing pentachlorophenate used for wood preservation. The sludge probably acts as a lipophilic absorbent for these substances. After extraction of the sludge, octachloro- and two heptachlorodibenzofurans were identified by means of mass spectrometry. The presence of the dibenzofurans may be explained by assuming that the technical pentachlorophenol was manufactured by catalytical chlorination of phenol, in the same way as for the lower chlorinated phenols. The identity of a predioxin with seven chlorines was also established, indicating tetrachlorophenol as a by-product in the formulation.

Analysis of Plankton

Boat bottom paint has been shown to contain PCB and pentachlorophenol and in addition high levels (about 1000 ppm) of chlorinated predioxins (PD 7 + PD 8). When plankton were sampled in the wake of a boat treated with the above-mentioned paint, analysis showed that the level, on a fat weight basis, of chlorinated predioxins was about 80 ppm (*3*).

Soil Analysis

Soil sampled from the surface layer in different saw mills contained chlorinated dioxins and predioxins in the range of 1–10 ppm, which is very high in relation to the content of chlorophenols.

REFERENCES

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